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(54) **Insect-resistant polymers**

(57) Small quantities of bifenthrin are used in formulations of plastic or polymeric compositions to provide compositions that are resistant to insect attack. The bifenthrin may be introduced as a component of a masterbatch which may be used to prepare PVC cable sheath.

Other polymers specified are polyethylene e.g. polyethylene wax and ethylene-vinyl acetate copolymers.

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BIFENTHRIN-CONTAINING POLYMER COMPOSITIONS FOR MAKING INSECT-RESISTANT CABLE

This invention relates to polymeric compositions useful for making formed plastic products which are resistant to attack by pests. More particularly, this invention relates to polymeric materials having incorporated therein an effective amount of bifenthrin insecticide which provides protection for cables against insect damage.

The practice of incorporating insecticides into plastics or polymeric materials such as polyethylene (PE), polyvinyl chloride (PVC), and copolymers such as ethylene/vinyl acetate is well-known. For example, flea collars for dogs and ear tags for cattle repel insects as a result of the release of the insecticide from the plastic and thereby protect the animal (US Patent No. 5,437,869).

In another application of insecticide-containing plastic, pyrethroid insecticides are incorporated into PVC cable sheath that insulates electrical wires (British Patent No. 1,538,222). Here, the cable sheath itself is the structure to be protected as it is susceptible to attack by underground termites. British Patent Application Publication No. GB 2,276,171A describes a masterbatch for making termite-resistant cable sheath. The masterbatch, containing cypermethrin dispersed in a copolymer of ethylene and vinyl acetate, is blended in a base polymer of polyethylene, ethylene/vinyl acetate copolymer or polyvinyl chloride. Cypermethrin in the blend at low concentrations is reported to deter termite attack.

Another pyrethroid, deltamethrin, has been reported to protect electric cable at low concentrations of deltamethrin. Due to the thermal stability of deltamethrin the plastic containing deltamethrin may be vulcanized, extruded or injected at temperatures up to 200 °C (Australian Patent Application No. 62173/90).

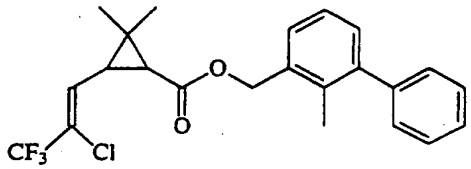
Also reported is a masterbatch of synergized pyrethrins wherein pyrethrum and piperonyl butoxide were incorporated into low density polyethylene granules (British Patent No. 1,568,936). This masterbatch containing about six percent of active ingredient was used to prepare films which were resistant to insect penetration.

In accordance with the present invention, it has now been found that bifenthrin insecticide at very low concentrations in certain polymeric compositions is useful in the protection of PVC cable sheath against attack by termites.

The present invention describes the use of bifenthrin in formulations of certain plastic or polymeric compositions useful for preparing PVC cable sheath thereby providing compositions that are resistant to insect attack. The bifenthrin is introduced as a component of a masterbatch. The masterbatch may be used directly to prepare a final composition. The final composition is suitable for compression and molding as in the PVC cable pipe preparations shown below.

The masterbatch of the present invention is prepared by mixing bifenthrin with polyethylene (PE) wax. The PE wax component is a low molecular weight polyethylene homopolymer having an average molecular weight range of between 1000 and about 4000, preferably between 2000 and about 3000 (available from Allied Signal Inc., Morristown, NJ, USA). A preferred PE wax is available from Allied Signal, Inc. under the name A-C 6A.

Bifenthrin is described in US Patent No. 4,328,505. Available from FMC Corporation, Philadelphia, PA, USA, bifenthrin is characterized as having very high insecticidal potency, good stability and as being relatively safe to handle (Farm Chemicals Handbook '95, Meister Publishing Company, Willoughby, OH). Bifenthrin has the following formula:



The relatively low human toxicity of bifenthrin, especially in relation to the amount necessary to prevent insect damage is a significant benefit in using it as an insecticide in plastic.

The concentration of bifenthrin in the masterbatch of the present invention may range from about 0.05 to 20 wt %. It has been found that the thermal stability of bifenthrin, which normally has a lower flash point than the temperature at which polyethylene is extruded, is enhanced when it is incorporated in the PE wax masterbatch. Technical grade bifenthrin has a flash point of 165 °C; however, bifenthrin as a 20 wt% component in PE wax was found to have a flash point of 213 °C. A masterbatch prepared from 20 wt% bifenthrin in PE wax has a melting point of about 110 to 125 °C. In a preferred embodiment for preparing PVC cable sheath, a masterbatch is obtained by mixing about 0.1 to 5 wt% bifenthrin in polyethylene wax. The bifenthrin/PE wax masterbatch can be readily ground into a powder for easy handling. Alternatively, a masterbatch may be prepared by mixing the bifentrhin with an additive, such as the Reofos described below.

For PVC cable sheaths, the bifenthrin/PE wax masterbatch is added to PVC resin so as to obtain 1 to 20 parts masterbatch per 100 parts resin (1 to 20 phr). This mixture or pre-blend is suitable for heat and compression shearing at temperatures ranging from about 110 to about 150 °C to form molded sheets that may be used for PVC cable. The bifenthrin concentration in PVC cable may range from 10 to 10,000 ppm. In a preferred embodiment, a masterbatch containing about 0.1 wt.% bifenthrin in PE wax is added to resin to obtain about a 5 to 20 masterbatch phr mixture. Such a mixture with the addition of various additives as described below contains bifenthrin in a

concentration of about 25 to 100 ppm. Bifenthrin concentrations as low as about 25 ppm are very effective in preventing attack by subterranean termites.

In addition to bifenthrin, there may also be included in the polymeric compositions of the present invention one or more additives conventionally employed in the art, as for example plasticizers such as triarylphosphates and dioctyl phthalate; fillers such as calcium carbonate and polyethylene wax; flame retardants such as PB370 (brominated phosphate ester) and antimony trioxide; or heat stabilizers such as tribasic lead sulfate.

EXAMPLE

For PVC pipe the following samples were prepared. From these samples were obtained molded sheets for activity testing.

Ingredient	Samples (as parts per hundred of PVC resin)				
	M 386	M 387	M 388	M 389	M 439
Polyvinyl chloride (PVC resin)	100	100	100	100	100
Reomol dop[1]	30	30	30	30	50
Reofos[2] 50 + 0.1% Bifenthrin masterbatch[3]	—	5	10	20	—
Reofos 50	20	15	10	—	—
Calcium carbonate	40	40	40	40	35
Tribasic lead sulfate	5	5	5	5	5
Calcium stearate	1	1	1	1	1
Antimony trioxide	—	—	—	—	5
Copper naphthenate	—	—	—	—	6

[1]Reomol dop = dioctyl phthalate
[2]Reofos = isopropylated phenyl phosphate
[3]Bifenthrin in Reofos 50

A series of tests were performed to evaluate the protection afforded the above prepared bifenthrin - containing polyvinyl chloride plastic material against attack by the subterranean termite *Coptotermeo curvignathus Holmgren*. These tests were carried out in the soil at Bogor, West Java, Indonesia, where these termites had been located and identified over a

period of eight years. For comparison purposes, a sample with copper naphthenate as the active ingredient was also prepared.

Test Methods

A concrete slab, 63 cm x 63 cm x 10 cm, was constructed on the ground surface as a "test unit." There were 25 test units in the field, arranged in 5 rows (distance between each unit was 80 cm). At the center of each test unit there was a 10 cm hole filled vertically by a PVC pipe, and one sample of test composition was put into the hole at ground surface.

Pine chips were laid around the test composition to attract the subterranean termites. The hole in the PVC pipe was then covered tightly.

Observations

Observations were conducted every two weeks for 24 weeks to identify: a) evidence of termite attack on the samples and wood bait; and b) the degree of protection of the test composition, using the scoring system identified below.

Degree of Protection	Score
Undamaged	100
Lightly Attacked	90
Moderately Attacked	40
Heavily Attacked	0

During the testing period it was observed that the colony of subterranean termite *C. curvignathus* had a very extensive foraging activity in the testing area, attacking most of lignocellulose materials on the ground surface. The termite tunnels could be found in bait wood in 76% of the test units. Even in the fourth week of evaluation, the bait wood in some test units was attached by *C. curvignathus*. The peak of termite infestation was in the eighth week, in which the bait wood in 48% of the test units was attacked.

Results

It was observed that during the sixth month, 80% of sample M 386 was attacked by subterranean termite *C. curvignathus* (mean of the degree of

protection was 72). It is believed that sample M 386 was very susceptible to the termite attack. During this time, 40% of samples M 387 and M 388 were slightly attacked (means of the degree of protection was 96). All samples of M 389 and M 439 were undamaged during the six month evaluation, even though the bait wood in the same test units was attacked by *C. curvignathus*.

The mean degree of protection of the samples are presented in the table below.

Compound	Conc. (ppm)	Sample	Degree of protection
Bifenthrin	0	M 386	72
	25	M 387	96
	50	M 388	96
	100	M 389	100
Copper naphthenate	3000	M439	100

*mean of five replications

It is apparent that various modifications may be made in the formulations and application of the present invention without departing from the inventive concepts herein, as defined in the claims.

What is claimed:

1. An insect-resistant polymeric composition characterized by an insecticidally effective amount of bifenthrin and a polymer selected from the group consisting of polyethylene, ethylene/vinyl acetate copolymers, and polyvinylchloride.
2. A composition of claim 1 further characterized by one or more additives selected from the group consisting of a triarylphosphate, isopropylated phenyl phosphate, dioctyl phthalate, antimony trioxide, calcium carbonate, tribasic lead sulfate, and calcium stearate.
3. A composition of claim 1 characerized in that the bifenthrin concentration is 10 to 10,000 ppm.
4. A composition of claim 1 characterized in that the bifenthrin concentration is 25 to 100 ppm.
5. A polymer masterbatch useful for preparing an insect-resistant polymeric composition characterized by an insecticidally effective amount of bifenthrin and a polyethylene wax homopolymer having an average molecular weight in the range between 1000 and 4000.
6. A masterbatch of claim 5 characterized in that the bifenthrin concentration is 0.05 to 20 wt.%.
7. A masterbatch of claim 5 characterized in that the bifenthrin concentration is between 0.1 and 5.0 wt.%.
8. An insect-resistant PVC cable sheath characterized by an insecticidally effective amount of bifenthrin, PVC resin, and one or more additives selected from the group consisting of a triarylphosphate, isopropylated phenyl phosphate, dioctyl phthalate, antimony trioxide, calcium carbonate, tribasic lead sulfate, and calcium stearate.
9. A cable sheath of claim 8 characterized in that the concentration of bifenthrin is between 10 to 10,000 ppm.

10. A cable sheath of claim 8 characterized in that the concentration of bifenthrin is between 25 to 100 ppm.

The Patent Office

9

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Claims searched:	1 to 10	**Date of search:**	12 September 1996

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Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.O): A5E ECC EL EN ES, C3K KPA, C3L LDA

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Other: ONLINE: CHABS, CLAIMS, JAPIO, RAPRA, WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X	GB 2276171 A BICC Public Limited Company see whole document	1,2,3,8,9

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.